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## AMMONIUM NITRATE EXPLOSIVE COMPOSITIONS

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This application is a continuation-in-part of our co-pending application Serial No. 671,383 filed July 12, 1957, now abandoned.

This invention relates to the preparation of explosives which are composed of mixtures of ammonium nitrate with a combustible substance.

Explosive compositions comprising mixtures of ammonium nitrate with dry combustible substances such as carbon black are known. These explosives are powerful in character but suffer from a number of limitations, and drawbacks. One major limitation is the necessity of using such explosives under conditions of close confinement in order to ensure that they fire. Thus, when these explosives are used for rock blasting, the explosives are usually put into a flexible container such as a bag which then must be tightly packed into a blast-hole; the blast-hole must be carefully drilled and free from cracks, fissures, and the like, so that the flexible container will conform as closely as possible to the configuration of the hole so as to fill it completely. In addition, various critical conditions are specified in connection with such explosives regarding the granulometric analysis of the explosive ingredients, the diameter of the bags used, and the spacing of the charge from the primer or detonator. Furthermore a homogeneous mixture of nitrate and carbon black has to be prepared at the place of manufacture in advance of use and there is hence the danger that the mixture may be exposed accidentally to firing conditions during storage or transportation. If saponifiable grease is admixed with such an explosive in an attempt to overcome this hazard, relatively complicated physical treatments which include drying, grinding and screening are required prior to use.

A general object of the invention is to provide explosives of this general character which will not have the limitations heretofore encountered.

More specifically, an object of the present invention is the production of improved explosive compositions prepared from ammonium nitrate and combustible ingredients, which will fire efficiently without the requirement of being placed in a confined condition and which will not require the observance of other critical specifications as to their conditions of use particularly as to the minimum diameter. Another object of the invention is the production of explosive compositions the ingredients of which may be stored and transported separately and mixed into a homogeneous composition immediately prior to use whereby a number of hazards are eliminated. A further object of this invention is to provide improved explosive compositions, the ingredients of which will not require extensive and complicated physical or mechanical treatment. Additional objects of this invention will become evident in the following description.

According to the present invention, a new form of ammonium nitrate is provided which has an especially porous, foam-like structure with a high power of adsorption. When this form of ammonium nitrate is mixed with a combustible material which is liquid and free-flowing, an explosive composition is formed that will fire efficiently under the action of a primer or detonator even in com-

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pletely unconfined conditions such as in free air. Of course, detonation of this explosive composition is even easier when it is in a confined condition. However, close confinement of this explosive is not a necessary requisite for the firing of this composition, so that the use of this explosive composition is facilitated and its range of applicability is greater extended.

The liquid ingredient in the explosive composition of this invention may be any of a variety of combustible liquids or mixtures thereof, including liquid hydrocarbon fractions such as gasoline, fuel oil, gas oil, and the like; alcohol, such as ethanol, methanol, and the like; and organic acids such as acetic acid and the like. The proportion of the liquid ingredient to the total weight of the composition that has been found satisfactory is from about 3% to about 12%, and a preferred range is from about 4% to about 8% by weight of liquid to the weight of the total composition.

The porous foam-like ammonium nitrate is prepared by evaporating a thin layer of a concentrated aqueous solution of ammonium nitrate in a crystallizer at reduced pressure. The ammonium nitrate foams up and solidifies rapidly under these conditions into an especially porous, expanded structure having the appearance of foam and a very low density. The crystalline form of the ammonium nitrate prepared in this manner usually corresponds to the normally observed crystalline form of ammonium nitrate. At ambient temperatures, that is at about 16° C. to 32° C. the ammonium nitrate is in the orthorhombic form common at this temperature. However, the lattice structure of the crystals is changed by this procedure and the relative positions of the crystals are modified so that there are a great number of cavities left between the crystals. The ammonium nitrate thus foamed and expanded has a high porosity and a considerable specific surface due to its unique structure, which also results in an ammonium nitrate which has a low density and a high adsorption.

In preparing this expanded and foamed ammonium nitrate, a solution of approximately 92–95% ammonium nitrate in about 5–8% of water at a temperature of about 140° C. is placed in a crystallizer. When, for example, a crystallizer is used which has a diameter of 1.40 meters, a height of 1 meter, and which is adapted to manufacture 100 kg. of foamed ammonium nitrate, about 68–70 cubic decimeters of solution is introduced into the apparatus, which produces a layer of solution of about 4–5 cm. depth. The crystallizer is then evacuated to a pressure of about 60 mm. of Hg and the water is evaporated quickly, which causes the ammonium nitrate to foam up. The ammonium nitrate foam thus produced is obtained as a cake which practically fills the crystallizer. The cake is then crushed and, if desired, the crushed particles are screened.

The porous nitrate may be prepared in accordance with any other method and it may be used in the form of porous granules. The particle size of the foamed ammonium nitrate is chosen for convenience, inasmuch as the size of the particles used is relatively unimportant and the outer shape of the expanded ammonium nitrate is of minor importance. The important feature is the unique expanded structure of the nitrate. Since the fuel penetrates the pores of the expanded, porous nitrate, there is no critical size for the particles. For ease in handling, slightly crushed particles of the foamed ammonium nitrate are generally used. However, the particles are crushed only to the extent necessary to obtain a convenient particle size, and the particles retain the stable, foamed structure.

Ammonium nitrate prepared in this way has an apparent bulk density, in gram per cc. varying from about 0.1 to about 0.85 and an adsorption coefficient of gas

oil of at least 8%. Ammonium nitrate having an adsorption coefficient of about 15% has been obtained. Since the adsorption phenomenon is a surface phenomenon, the rate of adsorption obviously changes with the density and the more the nitrate is expanded, the higher is the adsorption coefficient. By adsorption coefficient is meant the amount of liquid that can be adsorbed by the solid ammonium nitrate expressed in percent by weight of the liquid relative to the weight of ammonium nitrate.

As a result of the porosity and high adsorbency of the expanded ammonium nitrate, liquid fuel can be admixed therewith without particular agitation. However, if the explosive composition is prepared with agitation, mixing is effected more rapidly than when no agitation is used. No special mixing equipment is needed; any apparatus adapted to mix two substances, one of which is solid and the other liquid can be used. No particular precautions are required for the mixing operation other than normal safety precautions, such as avoiding open fires and avoiding temperatures above 150° C. for the ammonium nitrate. Since the mixing operation is simple, the two ingredients may be stored separately and combined only a short time before actual use. In this way the hazards of storing and shipping the explosive mixture are eliminated.

The liquid ingredients usable in accordance with the invention are widely available, inexpensive, and the amounts required are comparatively low. Moreover, suitable liquids for the purpose of the invention are inherently such that they will generally be found in large amounts on the work site, such as motor fuels. Hence, in many cases the preparation of an explosive, according to the invention will involve simply providing the foamed ammonium nitrate ingredients and bringing it to the site for use, where it may then be mixed with a suitable amount of liquid fuel just before the explosive is required. This is a great practical advantage.

Also as a result of the porosity, high adsorbency, and large specific surface of the foamed ammonium nitrate, the liquid combustible ingredient is well dispersed throughout the ammonium nitrate and coats a large amount of ammonium nitrate surface and it penetrates into the capillary ducts, so that a mixture of the foamed ammonium nitrate and fuel can be detonated relatively easily even in cartridges having a small diameter. As the ammonium nitrate is further expanded, detonation becomes easier. For example, in detonating an explosive mixture of 95% ammonium nitrate and 5% liquid fuel in a paper cartridge with a commercial number 8 primer which corresponds to 2 gr. of mercury fulminate if ammonium nitrate having a density of about 0.8 is used, the explosive mixture can be detonated in a paper cartridge having a diameter of 50 mm., if ammonium nitrate having a density of about 0.75 is used the explosive mixture can be detonated in a paper cartridge having a diameter of 40 mm., if ammonium nitrate having a density of 0.70 is used an explosive mixture can be detonated in a paper cartridge having a diameter of 30 mm., if the ammonium nitrate has a density of about 0.60 the explosive mixture can be detonated in a paper cartridge having a diameter of 25 mm., and the size of the paper cartridge can be reduced still further for lower densities, to about 20 to 22 mm. for a density of about 0.5. Consequently, the density should be chosen in accordance with the intended use. If small blast holes are provided, low densities should be used and for bigger blast holes higher densities should be employed. In order that the drilling of blast holes and the filling thereof be economical, it is advantageous to use the highest density which, for the diameter in question will lead to a safe and complete explosion. For general use, a density in the range of about 0.6 to about 0.75 is often preferable.

The adsorption coefficient of the ammonium nitrate may be increased by admixing with the nitrate a suit-

able amount of pulverulent carbonaceous material, such as carbon black, pulverized carbon, forms of cellulose such as soft sawdust and the like. This measure will at the same time prevent an undesirable setting of the ammonium nitrate. The maximum amount of carbonaceous material that should be admixed with the ammonium nitrate is the quantity which together with the combustible liquid ingredient just about completely utilizes the excess oxygen furnished by the ammonium nitrate.

Some examples will now be given of the practical procedure which may be followed in carrying out the invention, it being understood that the examples are illustrative but are not restrictive.

#### Example 1

1 kilogram of slightly crushed crystallized foamed ammonium nitrate (density not packed 0.654, density when packed 0.71, adsorption coefficient for gas oil 10%, well dried, water content 0.17%) is mixed with 70 grams of acetic acid and after 1 hour's rest the product is filled into shells, consisting of cardboard tubes having a diameter of 35 mm. Complete explosion is obtained with a No. 8 primer.

#### Example 2

A mixture is prepared of 1 kilogram of ammonium nitrate (light granules) having an apparent density of 0.420 without packing, and an adsorption coefficient of 15%, and 50 grams of diesel oil. After 1 hour's rest the mixture is filled into cartridges consisting of "kraft" paper having a diameter of 30 mm. and a weight of 100 g. The first cartridge is primed with a commercial No. 8-2 grams primer and is placed on a lead plate arranged on a support of sand. The second cartridge is equally placed on a lead plate, arranged on a support of sand. The extremities of the two cartridges are aligned, leaving a distance of 2 cm. between them. Explosion of the first cartridge is complete and entails the complete explosion of the second cartridge. The detonation rate of the second cartridge is 1,690 m. per second.

#### Example 3

A mixture is prepared of 1 kilogram of ammonium nitrate prills, well dried (apparent density without packing 0.76, density after packing 0.80, less than 0.1% water, adsorption coefficient 10.5) and 50 grams of diesel oil, having a density of 0.818. After a two hours' rest the mixture is filled into cartridges consisting of a cardboard tube having a diameter of 40 mm. and being primed with a commercial No. 8 primer. Explosion on a lead plate is complete.

#### Example 4

A mixture of 2 kilograms of ammonium nitrate prills, identical to the ones of Example 3, and 100 grams of ordinary gasoline is placed into a blasthole drilled in rock, having a diameter of 38 mm. and a length of 1.60 m. When an electric No. 8 primer is used, said mixture shows the same results as the same quantity of ammonium nitrate dynamite, whose blasting powder is 70% of the one of blasting gelatine.

The following is an example of tests carried out to illustrate the detonating qualities of the foamed, expanded ammonium nitrate.

#### Example 5

An explosive mixture consisting of 93% of foamed, crushed ammonium nitrate having a density of 0.36 and 7% gas oil was prepared by mixing with a wooden spatula. The mixture was screened through a No. 8 sieve and the screened particles analyzed to determine the average particle size of the ammonium nitrate with the following results:

14.5% of the particles have an average diameter greater than 1 mm.  
26% of the particles have an average diameter greater than 0.6 mm.

52% of the particles have an average diameter greater than 0.4 mm.

62% of the particles have an average diameter greater than 0.3 mm.

39% of the particles have an average diameter less than 0.3 mm.

The sieved mixture was introduced into sets of three tubular paper cartridge cases of 30 mm. diameter, of 52 mm. diameter and of 25 mm. diameter, the appropriate charge for each size cartridge case being used. The 30 mm. cartridge cases had a length of 15 cm. and when filled weighed an average of 51.5 gm.

To effect the detonation, three 30 mm. cartridges were aligned end to end on a lead sheet in the open air with the second cartridge spaced 1 cm. from the first and the third spaced 2 cm. from the second. Taking into account the thickness of the base of each cartridge case, the two intervals mentioned represented spaces of 2 cm. and 3 cm., respectively, between the explosive charges. Ignition was effected by means of a No. 8 detonator which corresponds to 2 gm. of pure mercury fulminate.

The three cartridges completely and properly detonated. Three regular furrows on the lead sheet showed that detonation of the three cartridges has propagated in proper manner.

When the above tests were repeated with two additional sets of 30 mm. test cartridges aligned in the manner of the first sets but provided with an additional 1 cm. spacing between adjacent cartridges, the results were the same, the cartridges leaving three regular furrows.

The two sets of 52 mm. cartridges were similarly tested and the results corresponded to those obtained with the 30 mm. cartridges.

The two sets of 25 mm. cartridges were then subjected to these same test procedures except that the distances between the adjacent cartridges were reduced by 1 cm. Again, the three cartridges detonated in perfect manner, leaving three regular furrows.

What I claim and desire to secure by Letters Patent is:

1. An improved explosive composition consisting essentially of 97%–88% porous ammonium nitrate foam having a bulk density of about 0.1 to about 0.85 and an adsorption coefficient for gas oil of at least 8% and about 3% to 12% of a liquid combustible material substantially adsorbed on said ammonium nitrate.

2. An improved explosive composition according to claim 1 wherein said liquid combustible material is a liquid hydrocarbon.

3. An explosive composition according to claim 1 wherein said ammonium nitrate foam is the evaporation product of a concentrated solution of ammonium nitrate evaporated at less than atmospheric pressure.

4. An explosive composition according to claim 1 wherein the quantity of said liquid combustible material corresponds to the amount of said material that can be substantially completely oxidized by the excess oxygen liberated by said ammonium nitrate when said ammonium nitrate is detonated.

5. An explosive composition according to claim 1, further comprising as an additional component, a combustible adsorbent material selected from the group consisting of carbon and cellulose.

6. An explosive composition according to claim 5, wherein the total quantity of said combustible adsorbent material and said liquid combustible material corresponds to the amount of said combustible materials which can be substantially completely oxidized by the excess oxygen liberated by said ammonium nitrate when said ammonium nitrate is detonated.

7. An improved explosive composition which consists essentially of about 88%–97% porous ammonium nitrate foam having a density of about 0.1 to about 0.85, an adsorption coefficient for gas oil of at least 8%, and a large specific surface, and about 3% to 12% of an organic combustible material substantially adsorbed on said ammonium nitrate, coating a large amount of the surface of said ammonium nitrate and filling the capillary ducts.

8. A stable explosive composition which consists essentially of about 88% to 97% of porous, expanded ammonium nitrate having a density of about 0.6 to about 0.75, an adsorption coefficient for gas oil of at least 8%, and a foam-like crystal or granular structure which has a large number of cavities among the crystals and thereby a large specific surface and about 3% to 12% of an organic-liquid, combustible material substantially adsorbed on said ammonium nitrate.

9. A method of preparing an improved explosive composition which comprises, evaporating a thin layer of concentrated ammonium nitrate solution at less than atmospheric pressure to obtain a stable porous ammonium nitrate foam having a density of about 0.1 to about 0.85, crushing said ammonium nitrate foam, and admixing about 88–97 parts by weight of said crushed ammonium nitrate foam with about 3 to 12 parts by weight of an organic, liquid, combustible material.

10. A method according to claim 9 wherein said liquid combustible material is a liquid hydrocarbon.

11. A method of preparing an improved explosive composition according to claim 9 and the additional step of storing said ammonium nitrate foam whereby said ammonium nitrate foam is admixed with said liquid ingredient just prior to use.

12. A method of preparing an improved explosive composition which comprises producing porous, expanded ammonium nitrate having a density of about 0.1 to about 0.85 and an adsorption coefficient of at least 8% by evaporating a thin layer of a 92% to 95% aqueous solution of ammonium nitrate at a temperature of about 140° C. and at a pressure of about 60 mm. of Hg, and admixing about 88 to 92 parts by weight of said expanded ammonium nitrate with about 3 to 12 parts by weight of a liquid, organic, combustible ingredient.

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